Synthesis & Characterization of 50BZT-50BCT Ferroelectric Ceramics by Combustion & Microwave Processing Routes

A thesis submitted in partial fulfilment of the requirement

For the degree of

MASTER OF SCIENCE

IN

PHYSICS

By

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis & Characterization of 50BZT-50BCT Ferroelectric ceramics by Solid state and Microwave Processing Routes"** submitted by Miss NISHA KUMARI SINGH in partial fulfilment for the requirement for the award of degree of Master of Science degree in Physics at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance in Electro ceramic Lab of Department of Physics.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or Diploma.

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I am also thankful to all the PhD scholars in the Electro Ceramic lab for their liberal co-operation with extending their all analytical facilities.

ABSTRACT

50BZT-50BCT has been prepared using conventional solid state reaction route and microwave synthesis route. Calcinations were done at 1000 ^{o}C, 1100 ^{o}C and 1200 ^{o}C. Sintering was done by the two reaction routes. For conventional method the sintering was done at 1300 ^{o}C, 1350 ^{o}C and 1400 ^{o}C. For the microwave synthesis method the sintering was done at 1300 ^{o}C for 20 minutes, 30 minutes and 40 minutes. Density and porosity measurement, XRD analysis, dielectric constant and dielectric loss measurement, SEM, P-E hysteresis loop and diffusivity measurements were done. Highest density was achieved in sample conventionally sintered at 1400 ^{o}C. XRD confirmed a perovskite tetragonal structure. Dielectric measurements were done in the frequency range 1kHz to 1 MHz. It showed a diffused phase transition. Maximum dielectric constant was found at the curie temperature.

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CHAPTER-1

INTRODUCTION

1. Introduction

Barium titanate is one of the most common but, at the same time, very important member of the "titanate family" due to its very high dielectric constant and ferroelectricity. It belongs to the perovskite family having the ABO_3 type structure where 'A' and 'B' represent the cation elements.

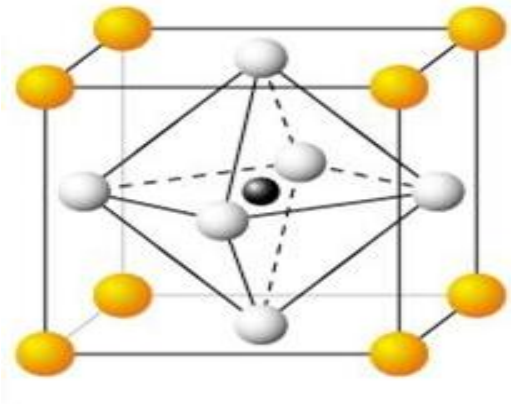


Fig. 1: Schematic diagram of perovskite (ABO_3) type structure [1]

If the yellow colored atoms sitting at the corners of the cube are considered as the 'A' type atoms then the black colored atom residing at the centre of the body is the 'B' type atom and the grey colored atoms lying at each face centre are the oxygen atoms. In case of $BaTiO_3$ structure the 'A' type atoms are the Barium atoms and the 'B' type atom is the Titanium atom.

1.1 Ferroelectricity

Ferroelectricity was first discovered in Rochelle salt (sodium potassium tartarate tetrahydrate) in the year 1921. Ferroelectricity is the property of certain materials which possess a spontaneous polarization that can be reversed by the application of an external electric field [2].

Due to their unusually high and unusually temperature dependent values of the dielectric constant, the piezoelectric effect, the pyroelectric effect, and electro-optical effects, including optical frequency doubling, ferroelectrics are of theoretical and technical interest[3].

These ferroelectric materials have a wide range of applications in various fields like high dielectric constant capacitors, piezoelectric SONAR and ultrasonic transducers, radio and

communication filters, medical diagnostic transducers, stereo tweeters, buzzers, gas igniters, ultrasonic motors, thin film capacitors, thin film ferroelectric memories etc[4].

1.2 Classification based on symmetry

In all there are 230 space groups and just 32 point groups. All the crystals can be divided into these 32 point groups. Out of these 32 point groups 11 are centrosymmetric, meaning the centre of positive and negative charge coincides with each other, whereas the rest 21 are non-centrosymmetric with one or more crystallographically unique directional axes[4].

1.3 Piezoelectricity

When a certain mechanical stress is applied on some materials, like crystals, ceramics, DNA and various proteins, they develop a charge in response to the applied stress. Such materials are called piezoelectric and the phenomenon piezoelectricity. The electrical charge developed is proportional to the applied stress. There are two types of piezoelectric effect.

a) Direct piezoelectric effect
b) Converse piezoelectric effect

Direct piezoelectric effect

In direct effect the mechanical energy is transformed into electrical energy due to the extension of the electric dipoles in the direction of the electric field, when the piezoelectric components are affected by an electric field [5]. Mathematically it can be expressed as:

$$P_i = d_{ijk}\,\sigma_{jk}$$

Where P_i is the polarization along the i-axis, σ_{jk} is the applied stress and d_{ijk} is the piezoelectric coefficient.

Converse piezoelectric effect

On contrary to the direct effect, in converse effect the electric dipoles get shortened on application of mechanical stress. This is because the piezoelectric components resist this trend so voltage is generated to keep the balance [5]. Mathematically,

$$\varepsilon_{ij} = d_{kij} E_k$$

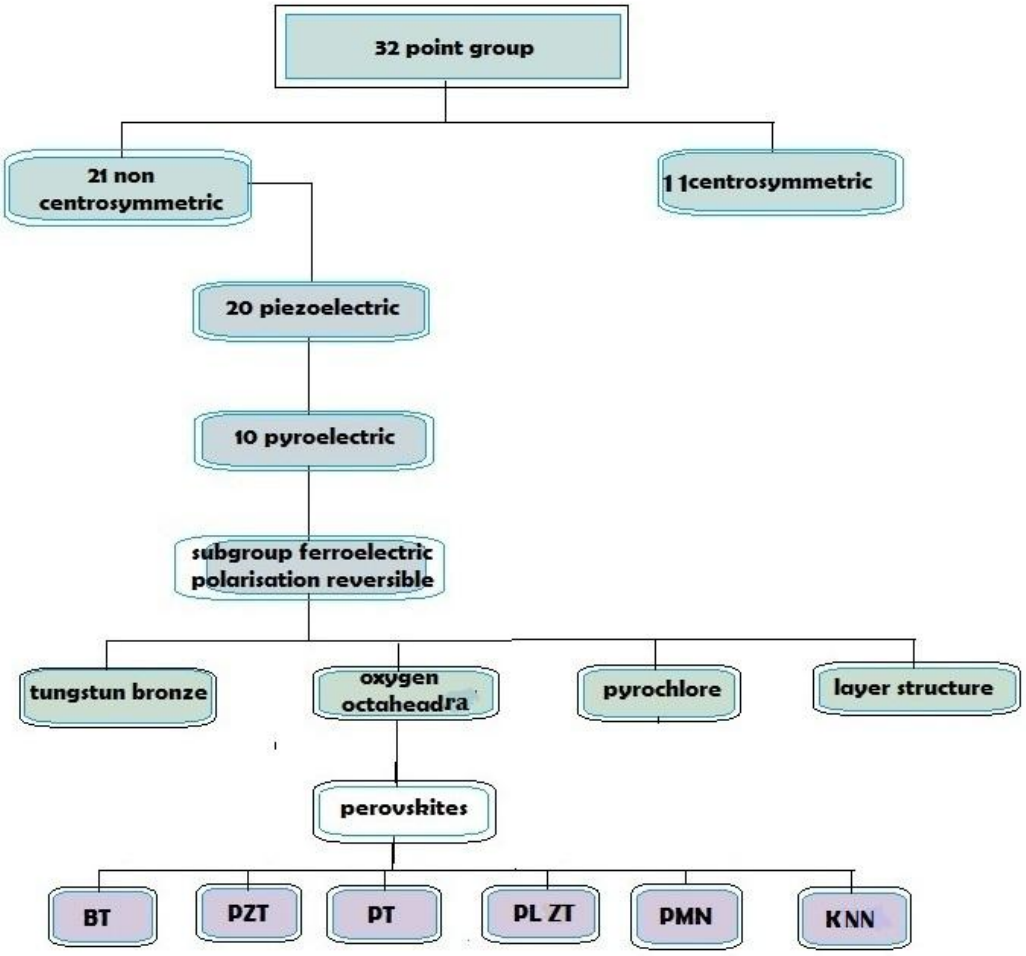
Where ε_{ij} is the strain generated in a particular orientation of the crystal and E_i is the applied electric field along the i-axis.

Production and detection of sound, generation of high voltages, electronic frequency generation, microbalances and ultrafine focusing of optical assemblies are some of the applications of these piezoelectric materials [6].

Out of the 21 non-centrosymmetric point groups 20 belongs to the class of piezoelectric. Out of these 20 point groups, 10 point groups are such that they have only one unique direction axis. These are called as pyroelectrics. In these crystals the ferroelectric dipole moment is not changed by the application of an electric field of the maximum intensity. Also in these types of crystals change in temperature causes a change in the spontaneous moment [3].

Flow chart showing the classification of point groups on the basis of symmetry

Fig.2



1.4 Substitution and modifications in BT system

Discovered by E. Wainer and N. Salomon in USA in the year 1942, by T. Ogawa in Japan in the year 1944 and by B.M. Vul in the year 1944 at Soviet Union, Barium titanate is the most common ferroelectric ceramic. It was first believed that it possess no piezoelectric property until

S. Roberts from USA in the year 1947 showed that after polling the material with a high DC voltage the desired piezoelectric properties are observed[7].

$BaTiO_3$ shows a series of phase transition varying from 120 $_0$C to -90 ^{0}C.

a) 120 ^{0}C and above – cubic phase
b) 5 ^{0}c to 120 ^{0}c – orthorhombic phase
c) -90 ^{0}c to 5 ^{0}c – rhombohedral phase

The phase transition from orthorhombic to rhombohedral phase, on decreasing the temperature, causes polarization along the [111] direction.

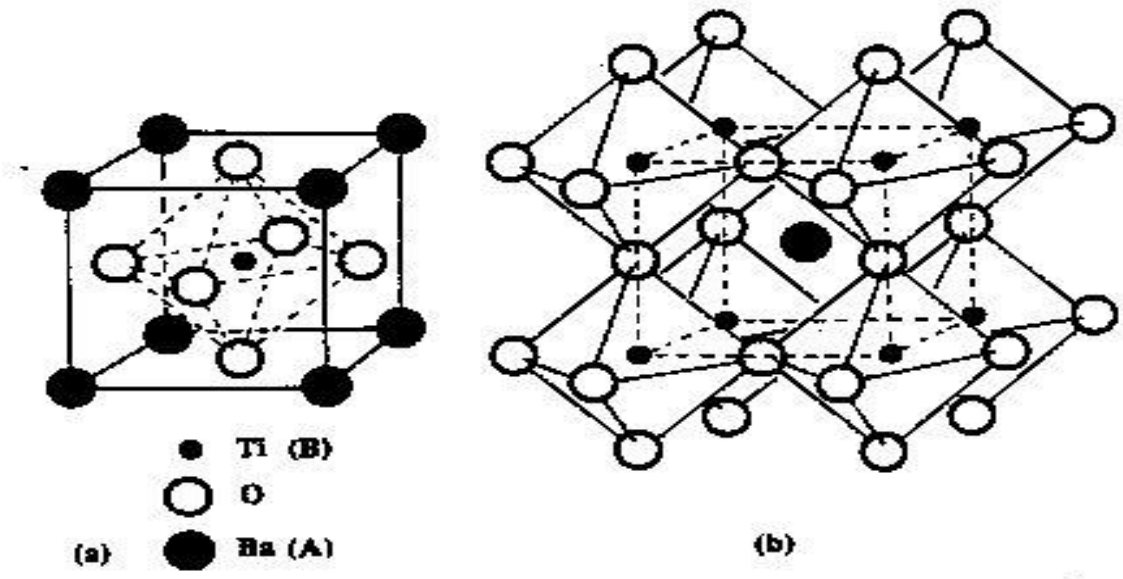


Fig.3: a) A $BaTiO_3$ unit cell (Perovskite structure - **ABO_3**) b) 3- dimensional network of corner sharing octahedra of O^{2-} ions. [4]

Barium titanate systems have very high dielectric constants due to which they are the material of first choice in manufacturing many electronic components like PTC thermistors, piezoelectric transducers and several electro-optic devices.

Despite of several advantages the BT ceramics have certain disadvantages too. One of the most important weak points noted about these ceramics is their poor temperature coefficient at resonance frequency. This is caused due to the second order phase transition just below the room

temperature. Secondly, it has got very low Curie point (~ 120 ^{0}C) which is responsible for excessive aging of the material [7].

To overcome these disadvantages various types of substituent like Zr, Ca, Sr, Pb etc, have been used and it is observed that these substituent can broaden, flatten or shift the phase transition characteristics of $BaTiO_3$. Sr substitution in place of Ba decreases the transition temperature whereas Pb substitution increases the transition temperature. Substituting Zr reduces the transition temperature and broadens the ε_r ~T curve. Experimentally it is found that ca ion can be substituted in both 'A' and 'B' sites of the perovskite structure.

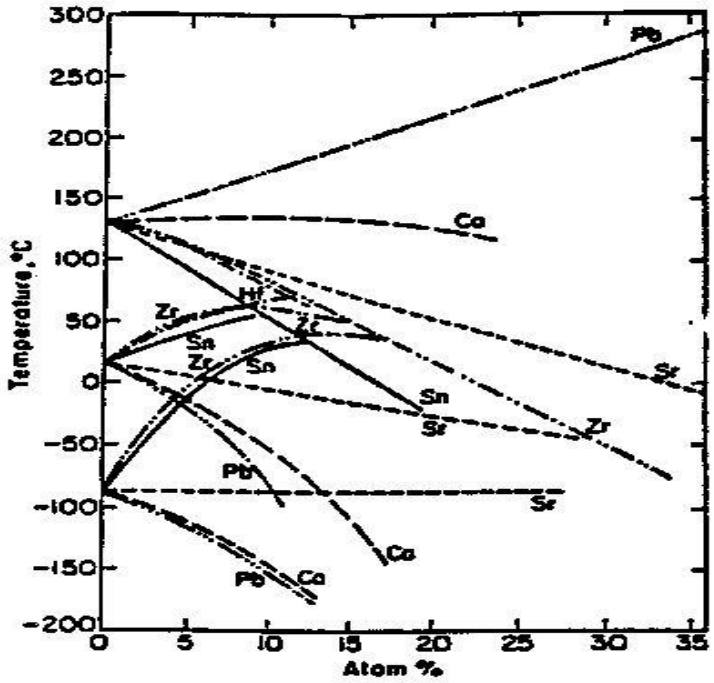


Fig .4: Effect of isovalent substitutions on the transition temperature of $BaTiO_3$ [4].

It is important to note that while substituting a particular cation the charge must be balanced and the ionic size should match with the coordination number of the cation which is being substituted otherwise the ionic mismatch may result in structure distortion of the crystal and hence the reduction in symmetry[8].

Literature Survey

Lead vs. Lead-free

Lead based ferroelectric ceramics have been at the forefront of ceramic industry since decades. This is due to their excellent dielectric, piezoelectric properties and electrochemical coupling coefficients. Apart from these properties one of the most interesting and important property of the lead based ceramics, that has fascinated researchers and scientists for a long time, is the presence of a morphotrophic phase boundary (MPB). In addition to this excellent electromechanical property is shown by compositions close to this boundary. As a result Pb-based ceramic families are the mainstay for high performance piezoelectric actuators, ultrasonic transducers, sensors etc. Their application ranges from small electronic industries to the high tech scanning tunnelling microscope and medical imaging.

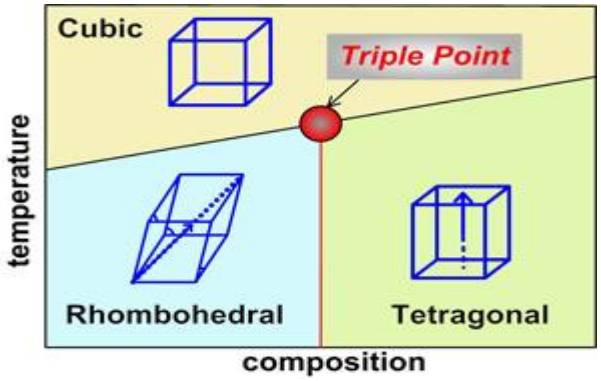


Fig.5 Existence of a triple point in the composition-temperature phase diagram for a Pb-based piezoelectric material [10].

Despite all these advantages Pb-based ceramics are facing global restrictions due to their high toxicity to environment as well as the human society. To be more precise, in the lead oxide based ferroelectric ceramics the lead oxide vaporises during processing but the lead remains in the environment for a very long time. Biological observations have revealed that it lead remains in the environment for a long time then there is a chance for it to get accumulated in the human body and cause damage to brain and nervous system [10,11,12,13]. So, to search for an alternative to Pb-based ceramic is the need of the hour.

Pb-free piezoelectric ceramics, however, have significantly lower piezoelectric and dielectric properties compared to the Pb-based families. Till now also it is a

matter of research why the piezoelectricity of non-Pb ceramics is so low. Significantly lower piezoelectricity is shown by Pb-free ferroelectric systems at the MPB. The advantage of using non-Pb ceramic is that it is eco-friendly and do not cause any harm to the environment. In addition to this, their low density is as an advantage in the underwater transducer applications for impedance matching. Due to their lower acoustical impedance they can also serve as an advantage in the medical imaging. Pb-free materials can also be used for a number of high temperature applications whereas Pb-based materials cannot be used for applications requiring higher temperature.

Why BZT-BCT?

The performance of Pb-free ceramics is only a fraction of the Pb-based ferroelectric ceramics. However, Wenfeng Liu from Jiaotang university in china and Xiabing Ren from national institute of material science in Japan have reported a Pb-free compound xBZT-(1-x)BCT , where 'x' is the molar percent, shows properties comparable to the best PZT known.

Liu et al. designed a non-Pb pseudobinary ferroelectric system $Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$. They investigated a full set of material constant for this compound and intrestingly they found a morphotrophic phase boundary (MPB) separating a ferroelectric R (BZT) and T (BCT) phase in the phase diagram. They also reported the existence of a C-R-T triple point which is not present in most of the Pb-free compounds and is a characteristic of Pb-based family. This showed that the mentioned compound has a high piezoelectricity comparable to those with PZTs. The most important thing they noted about the compound was the dependence of piezoelectric coefficient 'd_{33}' on position. d_{33} showed a maximum at this composition with a value (~560-620) pC/N which is comparable and in fact even higher than many soft PZTs [12].

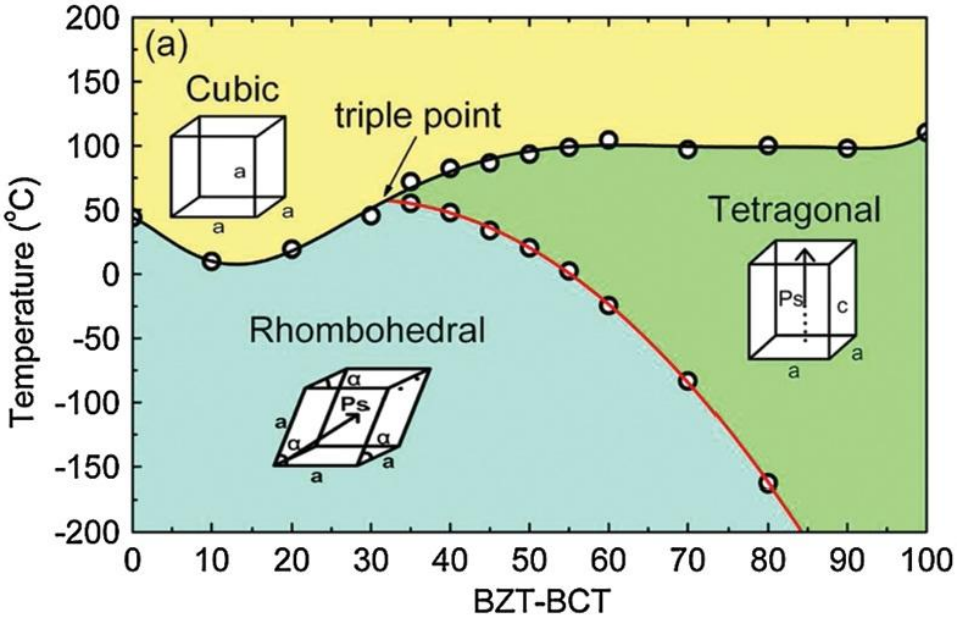


Fig.6 Phase diagram of pseudobinary ferroelectric system $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$[11]

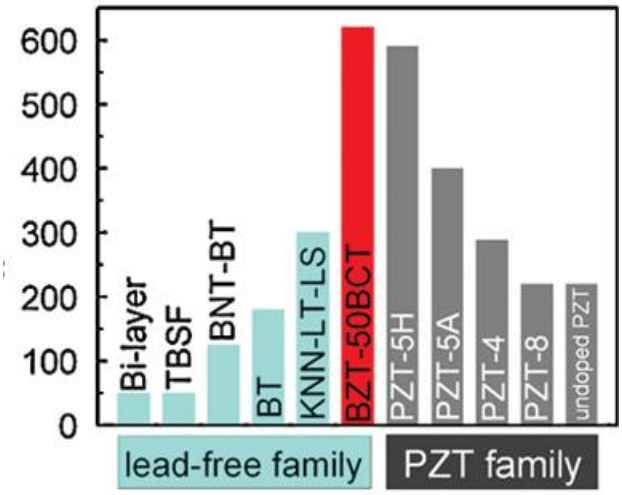


Fig. 7 Comparison of d33 among 50BZT-50BCT and other non-Pb piezoelectrics and PZT family [11]

Xue et al. prepared a composition (BZT-50BCT) by resonance method and investigated a full set of elastic, dielectric and piezoelectric properties. This method yielded the d_{33} value of 546 pC/N and a g_{33} value of 15.3 x 10^{-3} Vm/N, elastic constants s^E_{33}= 19.7 x 10^{-12} m^2/N and c^E_{33} = 11.3 x 10^{10} N/m^2 and electrochemical coupling factor was obtained to be of the order of K_{33} = 65%. Studying these values in detail it was found that these values were in close resemblance to the

properties of soft PZT materials. They reported that near MPB temperature these properties are optimal and deviation from the MPB temperature causes a decrease in these values. Even at -50^{0}C they observed a value of 93 pC/N for the piezoelectric coefficient d_{33}. Finally they compared the measured values of (BZT-50BCT) with the values of pure $BaTiO_3$ ceramics and soft PZT ceramics [13].

Wei li et al. reported the preparation of compound (($Ba_{0.93}Ca_{0.07}$) ($Ti_{0.95}Zr_{0.05}$)O_3) by solid state reaction route and studied all the properties of this compound with respect to the sintering temperature. In their experiment the samples were sintered at 1300 ^{0}C, 1350 ^{0}C, 1400 ^{0}C, 1450 ^{0}C and 1500 ^{0}C. On analysis they found that the samples which were sintered at 1450 ^{0}C had better densification and increasing the sintering temperature above this temperature results in a decrease in density of the material. In addition to this, this sample had also shown very high piezoelectric coefficient d_{33} = 387 pC/N and also a high curie temperature ~ 108 ^{0}C which is a greater than the reported value of 93 ^{0}C. It was observed that a little bit of rhombohedral phase as the secondary phase was shown by the sample that was sintered at 1300 ^{0}C. And there was a rapid decrease in the rhombohedral phase with increase in sintering temperature. They explained that the reason for decrease in rhombohedral phase is the diffusion of Zr and Ca in $BaTio_3$. The final conclusion that they drew from their work was that the above compound was showing very high dielectric and piezoelectric properties due to phase transition from orthorhombic to tetragonal phase [14].

Su et al. developed a composition of 50BZT-50BCT by solid state reaction route. First they weighed the raw materials according to the stoichiometry of the compound. The raw materials taken were $BaCO_3$, ZrO_2, $CaCO_3$ and TiO_2. Then the raw materials were thoroughly mixed by using a planetary mill in addition with alcohol for 12 hours. Then the mixture was again milled for 24 hours after calcining the ball milled mixture for 4 hours at 1350 ^{0}C. Then the resulting powder was taken out and pressed in the form of pellets without the addition of any kind of binder. The pellets thus prepared were sintered at different temperatures ranging from 1450 ^{0}C to 1500 ^{0}C. The heating rate was set to 5 ^{0}C/min during sintering. On XRD analysis of the sintered pellets it was found that the compound was showing a phase transition between rhombohedral and tetragonal phase. The Curie temperature was observed to be ~90 ^{0}C. The relative permittivity of the sample showed dependence on frequency. Finally, they concluded that the coexistence of phases at the MPB is the reason for such a high piezoelectricity [15].

Objective

The main objective of present work is to synthesize and characterise a Pb-free compound $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) where 'x' represents the molar concentration and is equql to 0.5 in this work process. The specific objectives are as follows:

a) To synthesize BZT-BCT by solid state reaction route and microwave processing route.
b) To study the effect of sintering temperature on the density of BZT-BCT ceramics.
c) To analyse the XRD patterns of the BZT-BCT ceramics.
d) To analyse the SEM images obtained.
e) To study the effect of temperature and frequency on dielectric constant and dielectric loss of the sample.
f) To study the ferroelectric and piezoelectric behaviour at room temperature.

CHAPTER-2

EXPERIMENTAL PROCEDURE

Procedure

Precursors, $BaCO_3$, ZrO_2, $CaCO_3$ and TiO_2 were taken in stoichiometric proportion for preparing 20 grams of $Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$.The quantities of these raw materials were measured using the electronic measuring machine correct up to 4 decimal places. These precursors were together ball milled for 6 hours using zirconia balls (powder to balls ratio 1:3) in acetone medium.

Then the mixed sample was taken out and after it got dry it was thoroughly grounded in agate mortar for nearly 1 hour so as to obtain a mixed powder of the raw materials. Then the sample was mixed with urea in the ratio 1:1. Urea acts as a fuel and during the reaction it burns without undergoing any reaction. After that the calcinations of the grinded sample was done at 1000 ^{0}C, 1100 ^{0}C and 1200 ^{0}C for 4 hours. The calcined powder was taken for XRD analysis. The XRD patterns of the calcined samples, at 1000 ^{0}C, 1100 ^{0}C and 1200 ^{0}C, were obtained at an angle of 2Ɵ with a scanning rate of 2^0 per minute from with a constant angular velocity from 20^0 to 70^0. After analysing the patterns obtained, the sample calcined at 1200 ^{0}C was chosen for sintering. The powder calcined at 1200 ^{0}C was taken and mixed with a binder that provides mechanical strength to the pellets to be formed from the calcined powder. Usually the binder used is poly vinyl alcohol. It is prepared by mixing vinyl alcohol in water and then stirring with the help of a magnetic stirrer for some time. The powder was taken and shaped in the form of pellets by uniaxially pressing with the help of dies for 2 minutes at a pressure of 6 atmospheres. The pellets were sintered at temperature 1300 ^{0}C, 1350 ^{0}C and 1400 ^{0}C using both solid state route as well as microwave processing route. In the microwave processing route the samples were sintered at 1400 ^{0}C for 20 minutes, 30 minutes and 40 minutes. The resulting powders were characterised by various characterisation techniques like density and porosity measurement, dielectric constant and dielectric loss, P-E loop and strain and SEM. Necessary graphs were plotted using the origin software. The measured values from both the synthesis routes were compared and analysed.

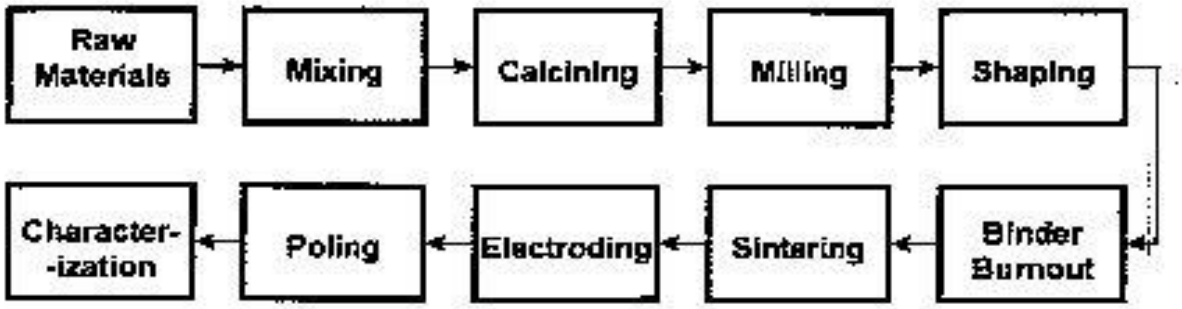


Fig .8 general flowchart for the processing of ferroelectric ceramics [4]

Synthesis

For the preparation of 20 grams of 50BZT-50BCT, the amounts of the raw materials used are as follows:

SAMPLE	MOLECULAR WEIGHT	QUANTITY USED
a) $BaCO_3$	197.35 g/mol	15.0465 grams
b) $CaCO_3$	100.09 g/mol	1.3467 grams
c) ZrO_2	123.22 g/mol	1.1053 grams
d) TiO_2	79.9 g/mol	6.4501 grams

These raw materials were mixed thoroughly using ball milling technique and then grinded in the agate mortar for nearly 1 hour so as to form a fine mixture of the mixed powders. Then urea is added to the sample in the ratio of 1:1 ratio. The molecular weight of urea is 60.06 grams/mol. Hence the amount of urea used for preparing 20 grams of the sample is 5.3874 grams. Urea acts an excellent fuel due to its lowest reducing power with total valences of +6. In addition to this it produces only 4mol of gases per mol of urea which is the smallest volume of gases produced. And the gases produced are also easily liberated. Furthermore, it is very cheap, easily and commercially available and generates the highest temperature. The uncontrolled REDOX REACTIONS containing such a fuel-rich mixture is generally exothermic in nature and may cause an explosion. But the same does not happen with urea-mixed powders because this produces an exothermic reaction that is not explosive. In addition to this, Urea also favours the preparation of powders without any hard agglomerates [16]. The mixture was then again mixed

with acetone and grinded in the agate mortar till acetone evaporates leaving the dry powder. The sample thus prepared is the raw BZT-BCT.

Calcination

After synthesis the powdered sample is heated or calcined in a tubular furnace for 4 hours at temperatures 1000 ^{0}C, 1100 ^{0}C and 1200 ^{0}C at a heating rate of 5 ^{0}C per minute. The furnace takes nearly 4 hours and some minutes to reach the desired temperature after which the temperature of the furnace became constant and the sample was calcined at the desired temperature for 4 hours after which the furnace was cooled and the sample was thoroughly grinded to ensure that there are no agglomerates in the sample. During the calcination process ferroelectric phase is obtained as a result of solid phase reaction between the constituents. The calcination temperature is very much important because it affects the electrical and mechanical properties of the ceramics to a large extent. If the calcination temperature is high then the homogeneity and the density of the resultant ceramic will also be high. Calcination temperature also affects the density and electromechanical properties of the ceramic product. So, one has to be very careful while deciding the calcination temperature [4].

Binder addition

The calcined sample at 1200 ^{0}C was chosen and mixed with polyvinyl alcohol that acts as a binder. The role of a binder is to provide mechanical strength to the pellets that are to be formed for sintering. Binder is made by mixing 2-3% of polyvinyl alcohol in powder form with distilled water and then stirring with the help of a magnetic stirrer. The binder vaporises during sintering. After mixing the binder the sample is left for sometime so that the mixture dries and then grinded again.

Pelletisation

For sintering the powdered sample was pressed in the form of cylindrical pellets of 0.5 grams each. The Pelletisation involves the uniaxial pressing using rigid dies with a pressure of 6 atmospheres. This method is also called as cold isostatic pressing.

Binder burnout

After shaping the powder in the form of cylindrical pellets, the pellets are heated at temperature around 600 ^{0}C so as to remove any binder present in the sample. The binder burnout rate was 2 ^{0}C/min so as to allow the gases to come out slowly from the ceramic sample without forming any cracks.

Sintering

The green pellets were then sintered in an indigenous programmable conventional furnace at 1300 ^{0}C, 1350 ^{0}C and 1400 ^{0}C with a heating rate of 5 ^{0}C per minute and at the same time the pellets were sintered using the microwave furnace for 20 minutes, 30 minutes and 40 minutes with a heating rate of 40 ^{0}C/min. Conventional sintering involves the reduction in free energy of the system that acts as a driving force for the process and is accomplished by atomic diffusion that leads to densification of the body. Microwave heating is volumetric and is fast and gives uniform and dense grain morphology.

Electroding

The sintered pellets were coated with silver paste and heated for 5-10 minutes to dry the coating and for good adhesion. The silver coating should be thin uniform and should adhere strongly to the ceramic. It should also posses zero resistance and good chemical and physical durability.

CHAPTER -3

CHARACTERISATION TECHNIQUES

X-Ray Diffraction (XRD)

XRD is an analytical and most common technique for the study of crystal structure nad atomic spacing. It is also used for the identification of phase of a crystalline material and also provides information on unit cell dimensions. It is based on the principle of interference. X-ray diffraction occurs when there is a constructive interference between the monochromatic x-rays and the crystalline sample.

X-rays to be used are generated by a cathode ray tube by heating a filament to produce electrons. These electrons are then accelerated with the help of an applied voltage towards the target material. Then these electrons are bombarded with the sample. Constructive interference is observed on the interaction of the electron beam with sample along with the production of a diffracted beam. When the geometry of the incident x-ray matches with the target material according to the Bragg's law of diffraction constructive interference occurs and a peak is observed in the intensity [17]. According to Bragg's law:

$$n\lambda = 2d \sin\theta$$

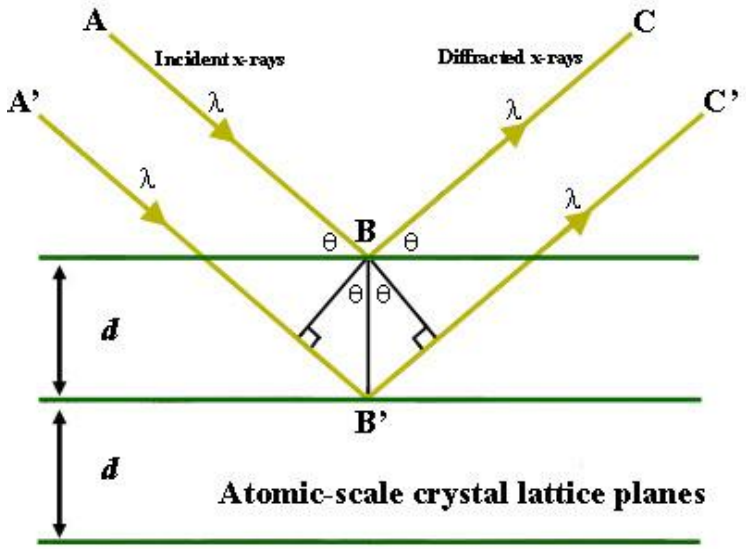


Fig. 9 Bragg's law of X-ray diffraction

The intensity of the reflected x-rays is recorded by rotating the sample and the detector. In the present work XRD was done using Philips analytical XRD machine with the wavelength of K-radiation = 1.5418 Å.

Density measurement

The density of the sintered pellets was measured using the Archimedes principle. In this method first the dry weight of the sintered pellets were taken using an electronic measuring machine. Then the pellets were immersed in kerosene and kept in a vacuum desiccator. As soon as vacuum started to fill inside the desiccator bubbles from the pellets started emerging out. These bubbles were the air trapped inside the pellets. It took about 1.5-2 hours for all the bubbles to come out. Then the beaker is taken out from the desiccator and suspended weight of the immersed pellet was measured by the density measurement kit and then soaked weight is measured. Finally the density and porosity were calculated as follows:

$$\text{Density} = \frac{\text{Dry weight} \times \text{density of liquid medium}}{\text{Soaked weight} - \text{suspended weight}}$$

$$\text{Porosity} = \frac{\text{Soaked weight} - \text{dry weight}}{\text{Soaked weight} - \text{suspended weight}}$$

Dielectric constant and dielectric loss measurement

For the measurement of dielectric constant and dielectric loss were done by electroding the samples with silver paste. The silver paste coated samples were heated at 500 ^{0}C so as to dry the silver paste on the pellets completely. The dielectric measurements of the sample were done by HIOKI 3532-50LCR HiTester instrument. The frequency range was varied from 1 Hz to 1 MHz. The dielectric properties were also measured as a function of temperature starting from room temperature. Then the data were extracted and plotted using the origin software to get the desired graph for dielectric constant and dielectric loss.

P-E Hysteresis loop

P-E loop is the characteristic property of the ferroelectric materials. When a ferroelectric material is subjected to an electric field the material is polarised. First the polarisation rises rapidly with the applied field and above this its behaviour becomes linear on application of field. If we

linearly extrapolate to y-axis, that is the zero field, it gives the saturation or spontaneous polarisation. On reducing the field to zero remanent polarisation is obtained. The negative field required to reduce the polarisation to zero is called as the coercive field. The hysteresis loop in ferromagnetic materials implies that there is a spontaneous polarisation in the material and depends upon a number of factors like the temperature, texture of the crystal, dimensions of the specimen and thermal and electrical properties of the material. The shape of the hysteresis loop of a ferromagnetic substance changes on increasing the temperature. With the increase in temperature the height and width of the loop also changes. At a certain temperature all the ferroelectric behaviour of the material disappears and the hysteresis loop merges to a straight line. This temperature is called as the "ferroelectric curie temperature"[18].

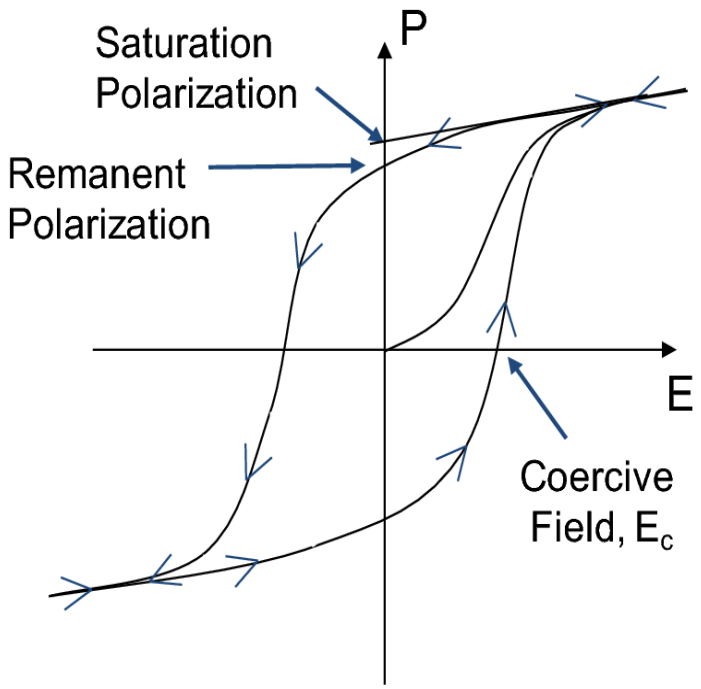


Fig. 10 Hysteresis loop of a typical ferroelectric material

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to study the microstructure and topographies of the sample. It scans the surface of the sample to build a 3-D image of the specimen with the help of electron beam. A typical SEM can magnify up to nanometre scale. The basic principle of SEM

involves the interaction of the electron beam generated from x-ray tube and the sample surface. This interaction generates a variety of signals. These signals include secondary electron, backscattered electron, X-rays, photons, heat and even transmitted electrons [19].

Backscattered electrons and secondary electrons are used for the imaging of the sample. Secondary electrons are used to study the topography and morphology of the sample whereas the back scattered electrons help to illustrate the contrast in the composition of multiphase samples. SEM most commonly comes in conjunction with EDAX [17].

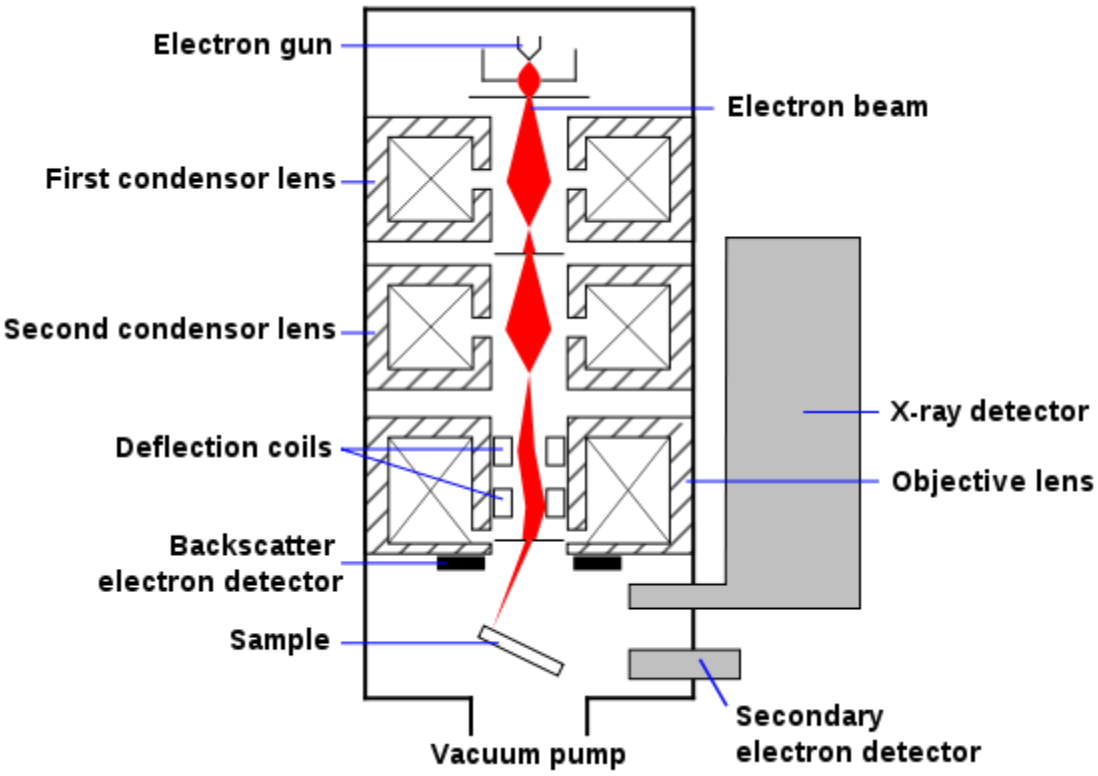


Fig. 11 Schematic diagram of a scanning electron microscope (SEM)

SEM has a wide range of applications ranging from the ceramic industry to the forensic lab. Through SEM observations can be done in macro and submicron ranges. It can be used in the forensic lab to investigate the gun shot residues. This is possible due to its ability of combining imaging with elemental analysis. When coupled with EDAX it can be used to determine the percentage compositions of different elements present in the compound.

CHAPTER-4

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The X-ray diffraction pattern of the sample calcined at 1000 ^{0}C, 1100 ^{0}C and 1200 ^{0}C was taken at an angle of 2Θ with a scanning rate of 2^0 per minute with a constant angular velocity from 20^0 to 70^0 . The figure below shows the XRD pattern of the sample calcined at the three temperatures.

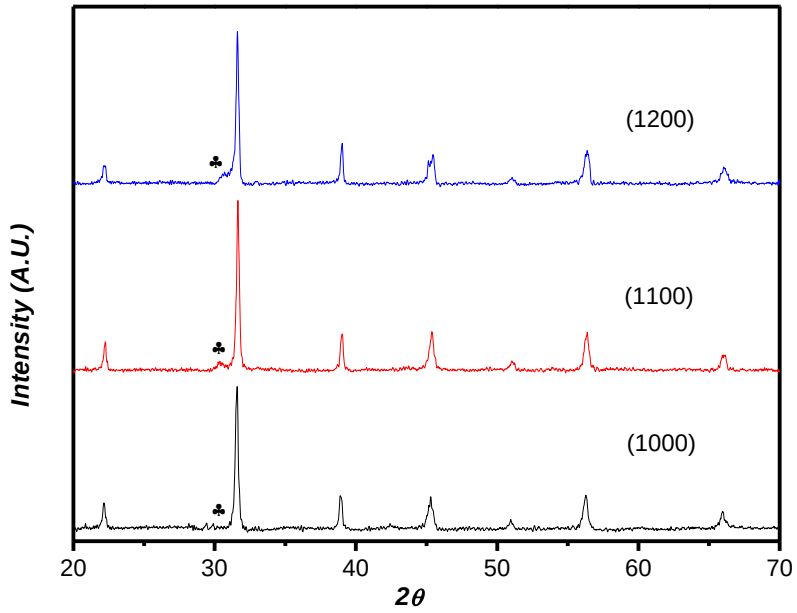


Fig .12. XRD patterns of 50BZT-50BCT calcined at 1000 °C, 1100 °C and 1200 °C

The pattern obtained was matched with the reference content in the expert database. The pattern confirmed the perovskite phase with tetragonal structure. The phase is completely formed at 1000 °C and as we increase the temperature the substance begins to melt that gives rise to a secondary peak in the XRD pattern. From the pattern it got clear that Calcium and Zirconium had diffused completely into the $BaTiO_3$ lattice to form a solid. 50BZT-50BCT showed a tetragonal structure.

SCANNING ELECTRON MICROSCOPE

The SEM images for samples were taken and their corresponding grain size was calculated using the linear intercept method.

FOR CONVENTIONAL SINTERING

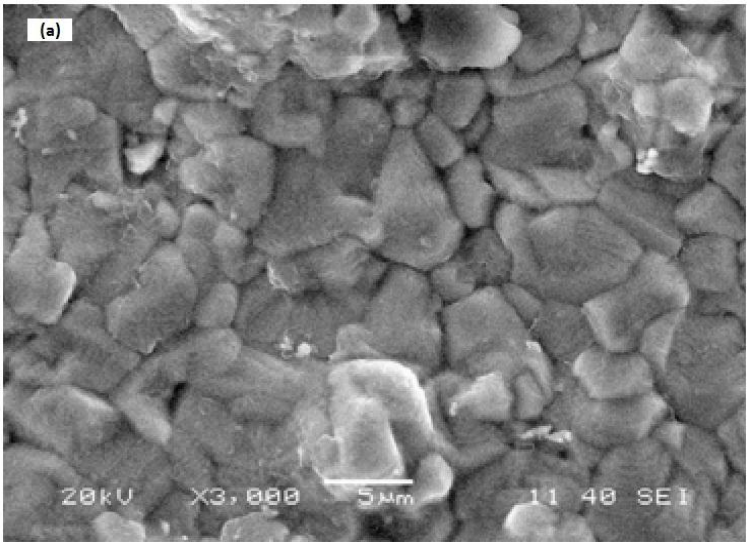


Fig. 22.SEM of sample Sintered at 1400 ^{o}C

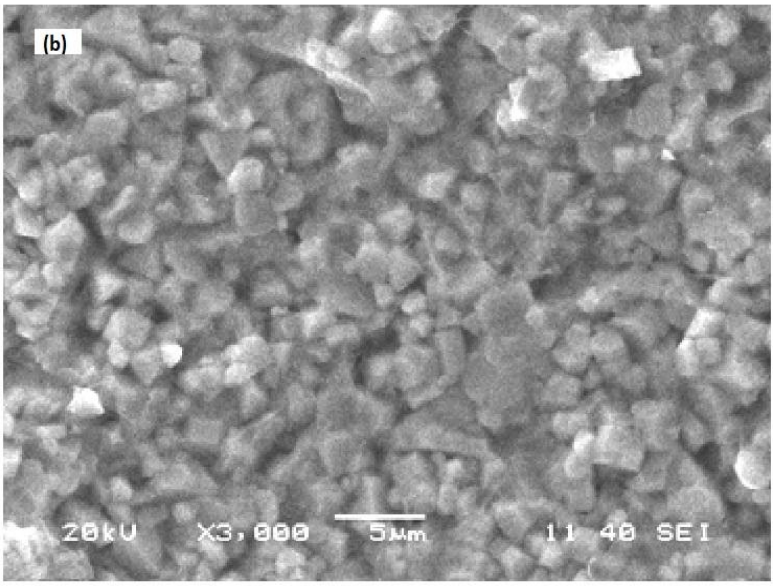


Fig .23 . SEM of sample sintered at 1350 ^{o}C

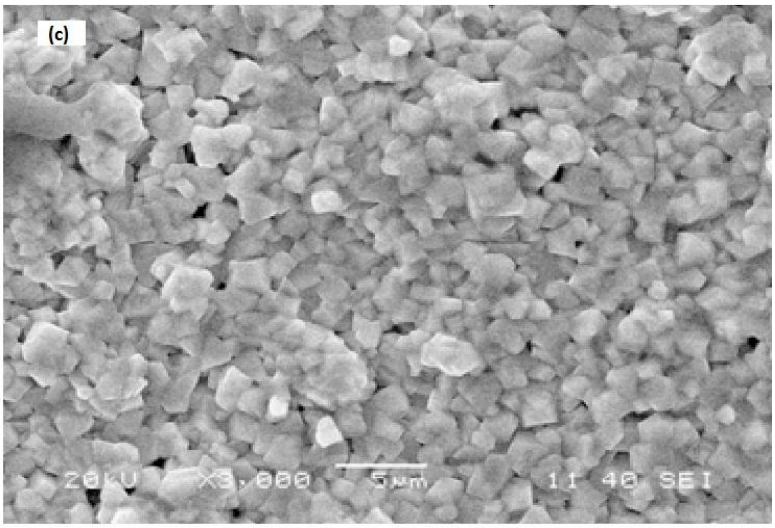


Fig . 24. SEM of sample sintered at 1300 °C

TABLE FOR CALCULATED GRAIN SIZE

SINTERING TEMPERATURE	CALCULATED GRAIN SIZE
1400 °C	~ 7.0048 μm
1350 °C	~ 4.0430 μm
1300 °C	~ 2.5526 μm

From the above table it is concluded that the grain size of the conventionally sintered samples increases with the increase in sintering temperature. The grain size increases with increase in temperature due to atomic diffusion.

FOR MICROWAVE SINTERING

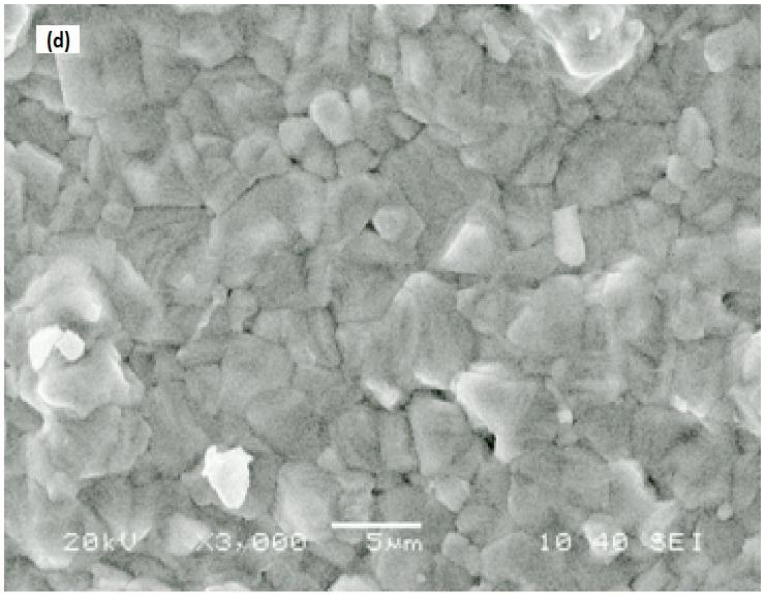


Fig. 25. SEM of sample sintered at 1300 ^{o}C for 20 minutes

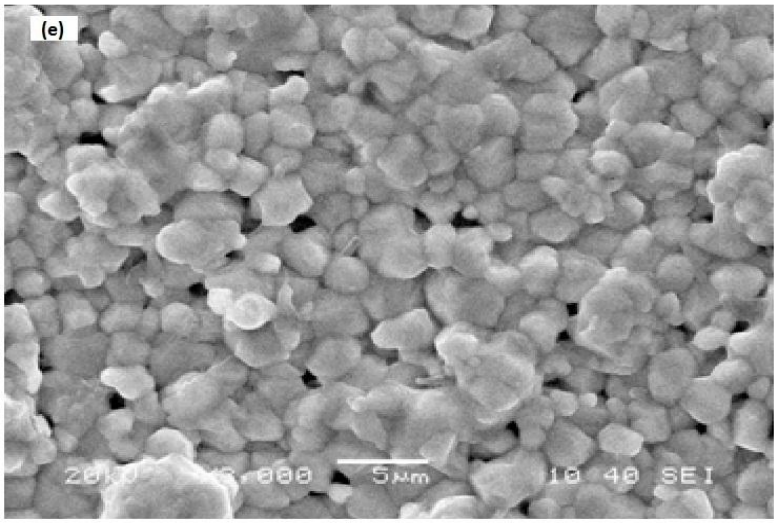


Fig .26. SEM of sample sintered at 1300 ^{o}C for 30 minutes

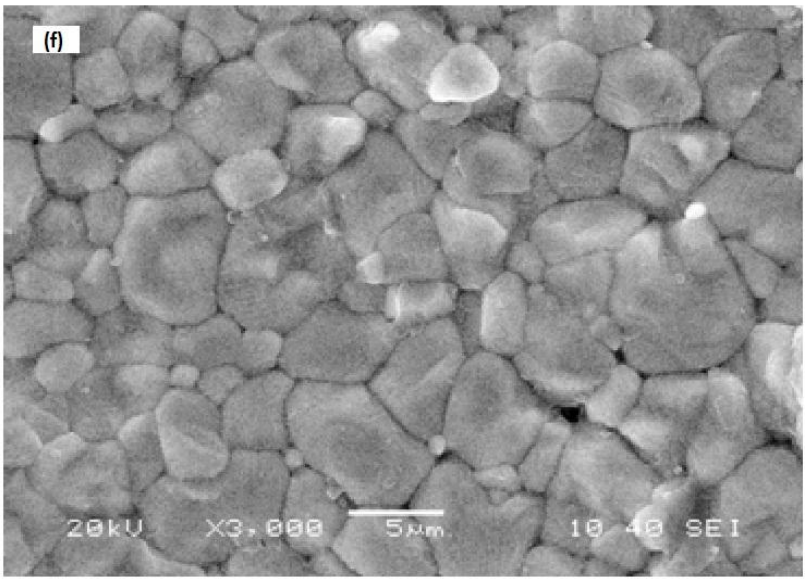


Fig .27. SEM of sample sintered at 1300 ^{o}C for 40 minutes

TABLE FOR CALCULATION OF GRAIN SIZE

SINTERING TEMPERATURE	CALCULATED GRAIN SIZE
20 minutes	5.0348 µm
30 minutes	6.4044 µm
40 minutes	8.6459 µm

From the above table it is interpreted that for the microwave sintered samples the grain size increases with the increase in temperature.

Density measurements

The density and porosity was calculated using Archimedes principle for both conventional and microwave sintered samples. The liquid medium taken was kerosene.

For conventional sintered:

SAMPLE SINTERED AT	DRY WEIGHT (g)	SOAKED WEIGHT (g)	SUSPENDED WEIGHT (g)	DENSITY IN g/cm^3	POROSITY %
1400 ^{0}C	0.4660	0.4662	0.3976	5.51	0.2
1350 ^{0}C	0.3951	0.3987	0.3377	5.25	1.8
1300 ^{0}C	0.4592	0.4605	0.3885	5.16	5.9

For microwave sintered:

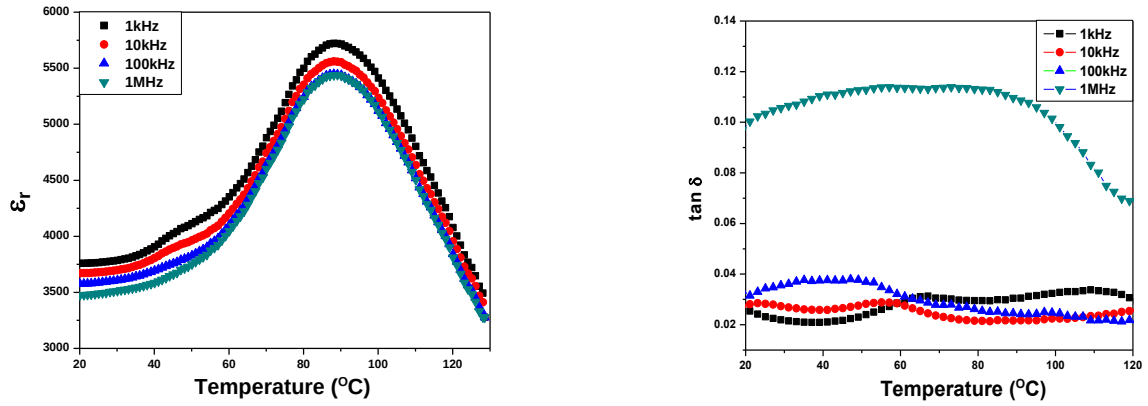
SAMPLE SINTERED FOR	DRY WEIGHT (g)	SOAKED WEIGHT (g)	SUSPENDED WEIGHT (g)	DENSITY IN g/cm^3	POROSITY %
20 MINUTES	0.4597	0.4664	0.3943	5.17	0.9
30 MINUTES	0.4603	0.4723	0.3957	4.9	1.5
40 MINUTES	0.4600	0.4701	0.3910	4.7	1.2

The highest density for 50BZT-50BCT was obtained to be 5.51g/cm^3. The density in conventional method was found to be highest for the sample sintered at 1400 ^{0}C followed by the samples at 1350 ^{0}C and 1300 ^{0}C. And for microwave method the highest density was found for sample sintered at 20 minutes followed by 30 minutes and 40 minutes.

Dielectric measurements

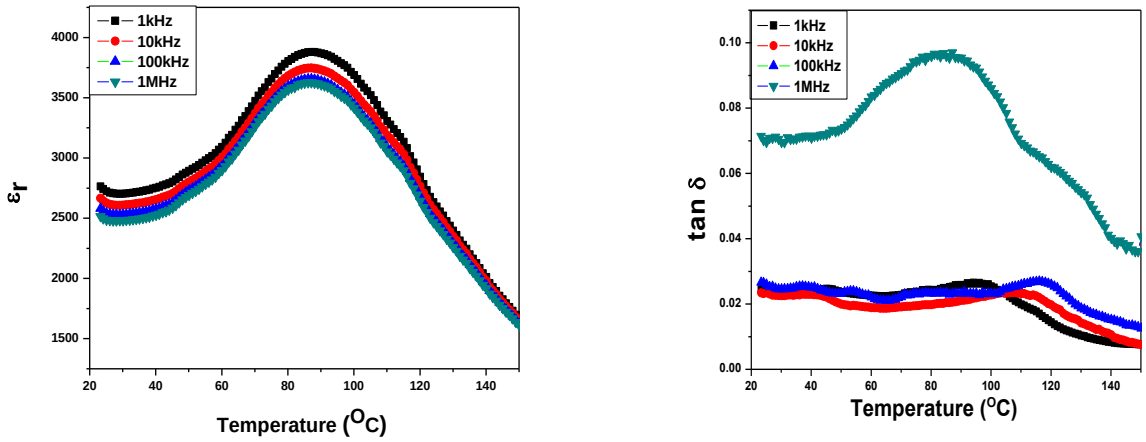
The dielectric loss and dielectric constant were measured using the instrument HIOKI HI-TESTER 3532-50 for both the conventional and microwave sintered pellets and the data obtained was used to plot the respective graphs using the software called origin. The figures below show the variation of dielectric constant and dielectric loss with temperature for both microwave and conventional sintered samples.

CONVENTIONALSINTERING:



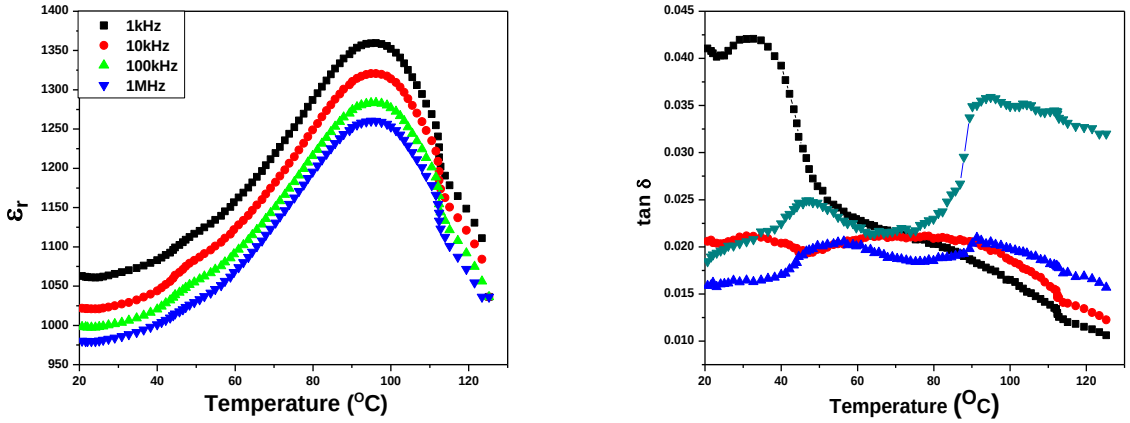
(a) (b)

Fig.13. Variation of (a) dielectric constant and (b) dielectric loss with temperature for sample sintered at 1400 ^{o}C.



(a) (b)

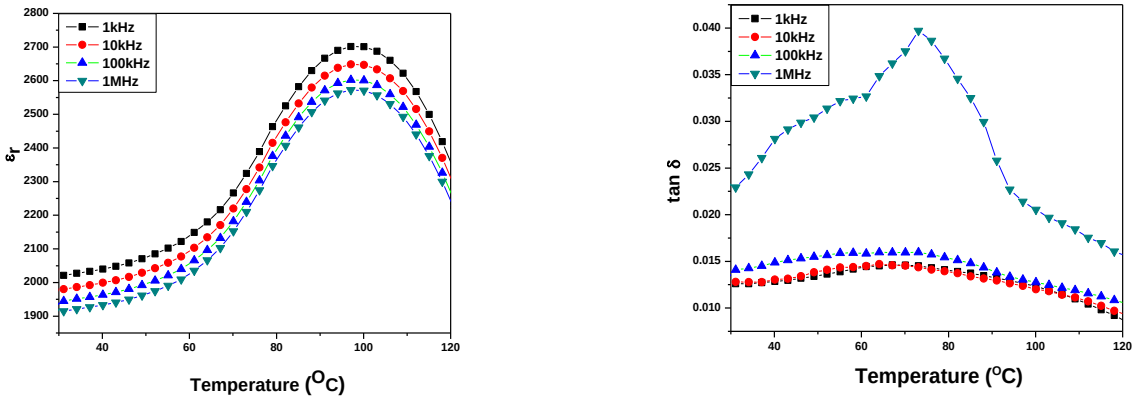
Fig.14. Variation of (a) dielectric constant and (b) dielectric loss with temperature for sample sintered at 1350 ^{o}C.



(a) (b)

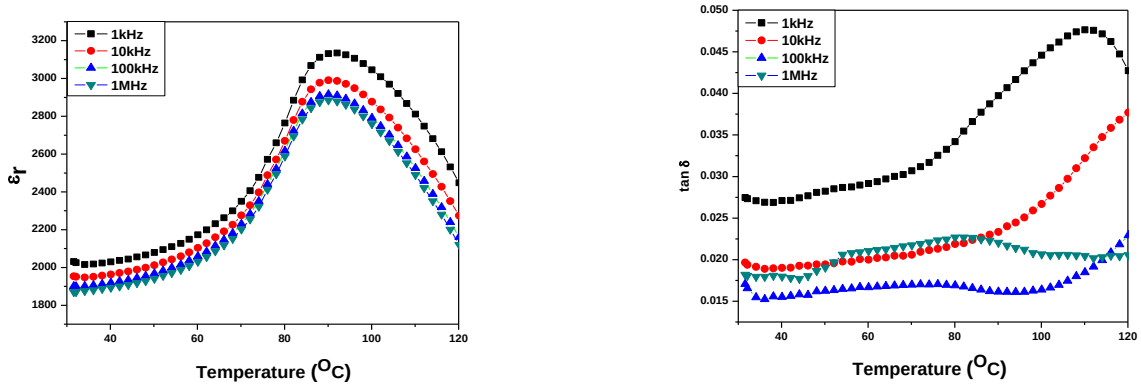
Fig.15. Variation of (a) dielectric constant and (b) dielectric loss with temperature for sample sintered at 1300 °C.

FOR MICROWAVE SINTERED



(a) (b)

Fig.16. Variation of (a) dielectric constant and (b) dielectric loss with temperature for sample sintered at 1300 °C for 20 minutes.



(a) (b)

Fig.17. Variation of (a) dielectric constant and (b) dielectric loss with temperature for sample sintered at 1300 °C for 30 minutes.

The values of dielectric constant (ε_r) at 1 kHz for the conventionally sintered samples are ~ 3765, 2723, 1060 and the values of dielectric loss at 1 kHz are 0.0147, 0.0242, 0.0402 at room temperature 25 ^{0}C for samples sintered at 1400 ^{0}C, 1350 ^{0}C and 1300 ^{0}C, respectively. The value of dielectric constants for microwave samples sintered at 1300 ^{0}C for 20 minutes and 40 minutes are ~ 2018, 2031 and the values of dielectric loss are 0.0128, 0.0275 respectively.

The value of dielectric constant increases with increase in temperature up to a certain temperature called the critical temperature after which it starts decreasing with further increase in temperature indicating a phase transition from ferroelectric to paraelectric phase. Dielectric constant increases with increase in temperature due to increase in polarisation caused because of separation of negative and positive charges at higher temperature. This is called as displacive transition.

P-E HYSTERESIS LOOP

The hysteresis loop for the conventionally sintered samples was studied. The saturated polarisation, the spontaneous polarisation, applied electric field and remnant polarisation were studied by the polarisation mechanism.

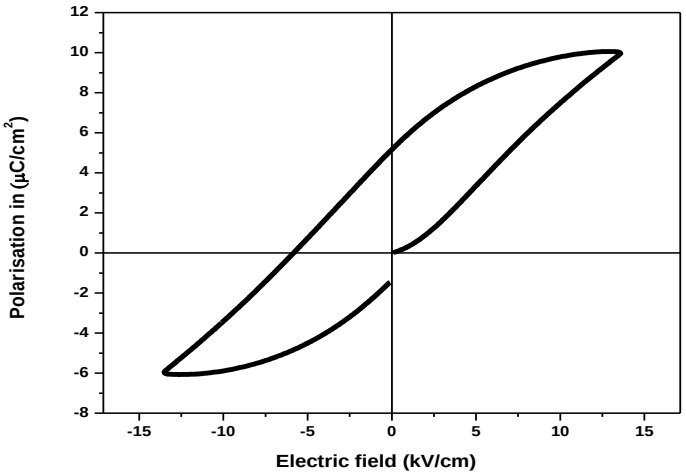


Fig.18. Hysteresis loop for the sample sintered at 1400 °C

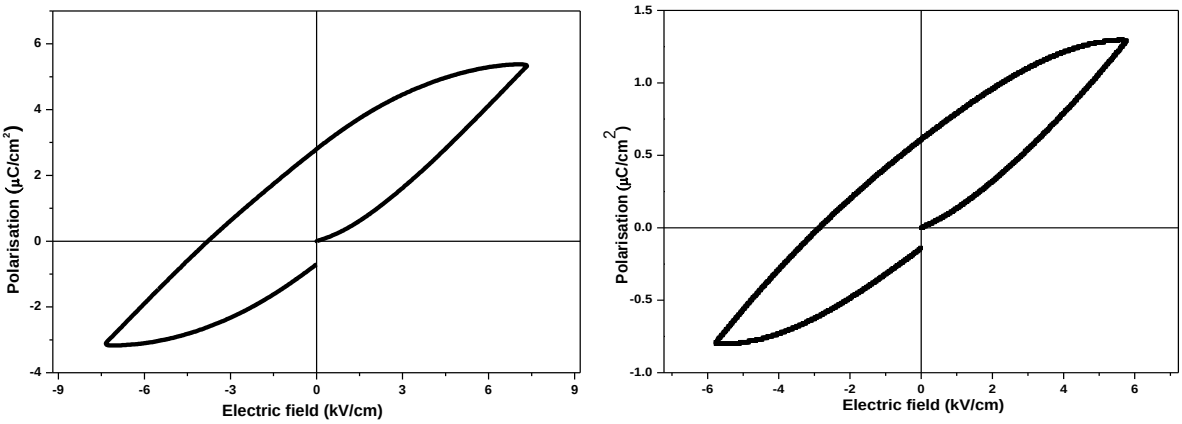


Fig .19. Hysteresis loop for sample sintered at, (a) 1350 °C and (b) 1300 °C

For this the maximum value of polarization at 1400 ^{o}C is P_{sat} = 10.5 μC/cm^2 , P_r = 4.34 μC/cm^2 and the value of coercive field is E_c = 490 kV/cm. The maximum value for polarisation at 1350 ^{o}C is P_{sat} = 4.22 μC/cm^2, P_r = 1.75 μC/cm^2 and the value of coercive field is E_c = 315.23 kV/cm and that for sample sintered at 1300 ^{o}C is P_{sat} = 1.04 μC/cm^2, P_r = 0.375 μC/cm^2 and the value of coercive field is E_c = 296.065 kV/cm.

The P-E loop becomes thinner and sharper as temperature is increased.

DIFFUSIVITY

The ability of a substance or a material to undergo or permit diffusion in it is called as diffusivity of the material. It is calculated to confirm the phase transition and varies from 0-2. If diffusivity lies in between:

0-1- It signifies a first order phase transition. In a first order phase transition there is a sharp increase or decrease of dielectric constant at the phase transition.

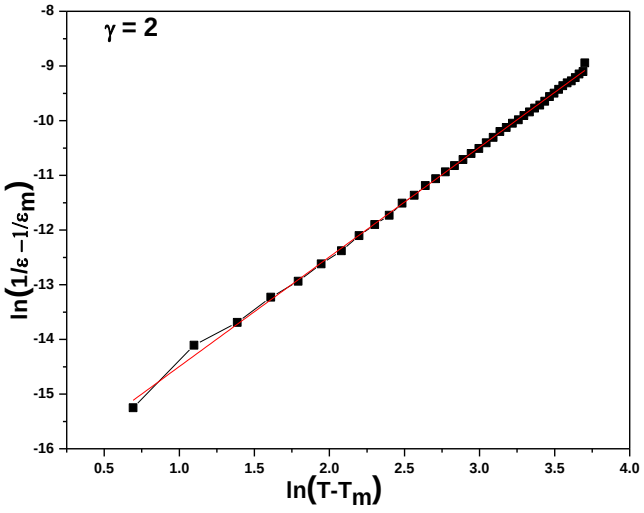
1-2- It signifies a second order phase transition or diffused phase transition. Diffused phase transition occurs due to microscopic inhomogenity in the material.

Diffusivity can be calculated by

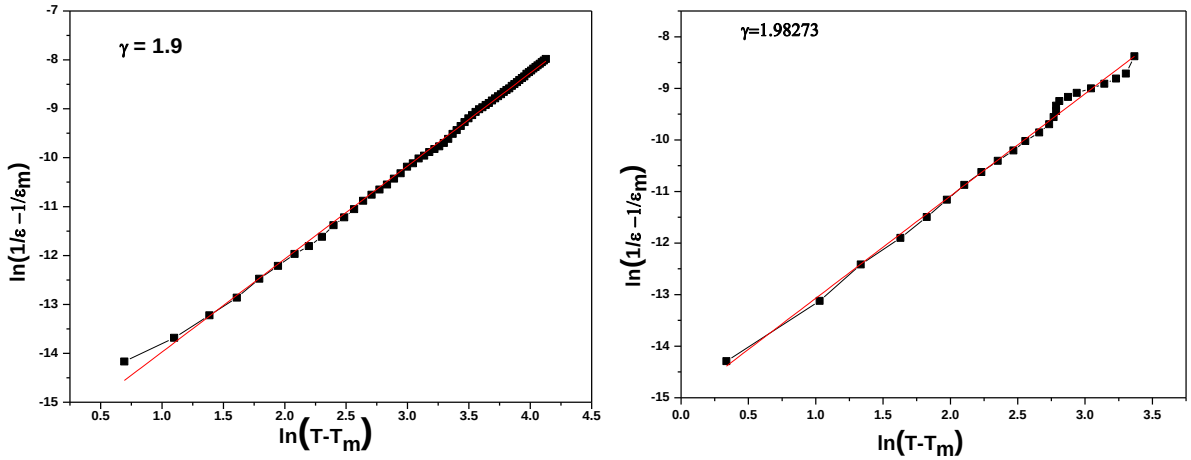
$$\ln (1/\varepsilon - 1/\varepsilon_m) = \ln (T - T_m)$$

The diffusivity for conventional and microwave sintered samples were plotted.

For conventional sintered



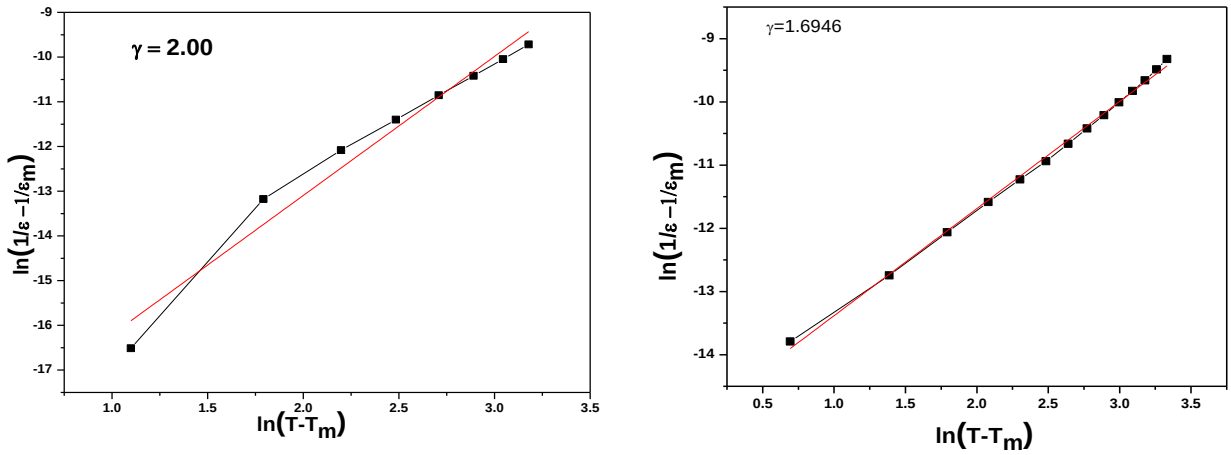
(a)



(b) (c)

Fig.20. Diffusivity for samples conventionally sintered at (a) 1400 ^{0}C, (b) 1350 ^{0}C and (c) 1300 ^{0}C.

FOR MICROWAVE SINTERED



(a) (b)

Fig.21. diffusivity of microwave samples sintered at 1300 ^{o}C for (a) 20 minutes and (b) 40 minutes

CONCLUSION

The sample 50BZT-50BCT was prepared using the conventional solid state reaction route and microwave synthesis route. At lower calcination temperature of 1200 ^{o}C pure BZT-BCT phase can be prepared. XRD pattern of 50BZT-50BCT ceramic indicates the perovskite phase with very small or negligible impurity phases. Density, dielectric and piezoelectric properties were measured for 50BZT-50BCT ceramics. Density was highest for the sample sintered at 1400 ^{o}C in case of conventionally sintered process and in case of microwave route the density was highest for the sample sintered at 1300 ^{o}C for 20 minutes. These ceramics are potential candidates for the lead-free piezoelectric application. The average grain size ranges between 2-8 μm.

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